ELECTROLYTIC POLISHING OF NON-FERROUS METALS

by

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B. S., Kansas State College
of Agriculture and Applied Science, 1951

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Shop Practice

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1951

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INTRODUCTION

Electrolytic polishing is in essence the reverse process of electroplating. In the electroplating process the object to be plated is made the cathode (negative electrode) of a source of direct current in an electrolytic solution which is made of a salt of the metal to be deposited. The anode (positive electrode) is made of the metal to be deposited or of an inert material. In the electropolishing process, on the other hand, the object to be polished is made the positive electrode of a direct current source in a proper solution. The negative electrode may be of any other conductive material which is not attacked by the electrolyte being used. When the direct current is applied, the protruding ridges or high points are dissolved and the surface of the object becomes smooth and bright.

Theory

At present there are two theories concerning the mechanism of electrolytic polishing. According to one of the theories the polishing action is caused by the formation of a viscous film which adheres to the surface of the metal. This viscous film being thicker in the depressions than on the protruding ridges protects the surface of the depressions while the protruding ridges dissolve away. According to the other theory the polishing action is caused by the concentration of metal ions in the

depressions. As the metal goes into solution it gives up positive ions. These ions flow away from the protruding ridges on the surface of the object, but accumulate in the depressions. This accumulation of positive ions prevents the surface of the depressions from going into solution while the unprotected protruding ridges dissolve away.

Advantages of Electrolytic Over Mechanical Polishing

Electrolytic polishing has at least four advantages over mechanical polishing.

Ease of Operation. In order to obtain a uniformly smooth finish by mechanical polishing, the operator must be very skillful. For each electrolytic polishing job such variables as solution composition, temperature, current density, polishing time, and previous preparation of the sample must be carefully worked out. After this has been done for a particular metal, however, the polishing procedure is quite simple, especially if automatic or partially automatic equipment is used.

Time of Operation. Depending upon the size and shape of the specimen, a mechanical polishing operation may take anywhere from 15 minutes to 1 hour after the initial preparation of grinding through 3/0 grit size emery paper. The same degree of finish, or perhaps better, may be attained in as short a time as 20 seconds, depending upon the material to be polished and solution used.

Polishing Recesses. By the electrolytic polishing method it is possible to polish in recesses and depths which are not normally accessible to mechanical polishing wheels. The electrolytic method does not require a plane surface to obtain a good finish.

Distortion of Crystal Lattice. The fact that the electrolytic method of polishing does not flow the surface metal is particularly important when the polished specimens are to be used for metallographic examinations. When metals are polished mechanically, the abrasive particles produce a thin superficial layer which has lost its crystalline form. Thus, if this layer is not removed during the etching, the microscope does not reveal the true structure of the metal. Mechanical polishing also causes the metal to flow, covering pits and inclusions, Plate V.

SURVEY OF LITERATURE

The first recorded observation of electrolytic polishing appeared about 1925 (35, p. 5). It was a reference by Madsen who at that time was working on the production of high-quality electrodeposited nickel on steel. While he was using a bath containing concentrated sulfuric acid at a current density of about 100 amperes per square feet in order to obtain satisfactory adhesion to the steel, he noticed that this resulted in the production of a white pearly surface on the steel. About

three years later two other investigators, Burns and Warner (4), took out a patent for an anodic electrocleaning process. As electrolyte they used 70 to 100 per cent phosphoric acid.

In 1930 Laban, according to Wernick, (35, p. 5) noticed the production of a clean satin finish on steel resulting from an anodic treatment in a 30 per cent sulfuric acid bath to which a small quantity of potassium dichromate was added.

In 1932 Hogaboom (18) took out another patent for the process which he called Electrolytic Bright dipping on iron and steel. This process consisted in making cathodically descaled steel the anode in a sulfuric acid bath of 25 to 75 per cent concentration. According to Hogaboom, the steel surface was brightened through the local formation of persulfuric acid.

The next important work in the field of electropolishing was made by Jacquet, according to Wernick, (35, p. 6) who studied the phenomenon of electrolytic polishing from 1935 onwards. He obtained mirror finishes on copper using an orthophosphoric acid electrolyte. Later, he worked with other common metals and developed a number of electrolytes (35, p. 7) of acetic and perchloric acids in various proportions to suit a particular metal. In his studies Jacquet was concerned only with the application of electrolytic polishing to metallographic purposes. Although he obtained very good results, especially on steel and copper, with the perchloric acid-acetic anhydride electrolytes, his process did not develop along commercial lines because of the hazards involved. The perchloric acid-acetic anhydride

mixture becomes explosive under certain conditions (31, p. 98).

The development of stainless steel provided a useful and practical application for electrolytic polishing methods. Stainless steel is very difficult to polish mechanically because the high pressure that it requires plus its low thermal conductivity tend to cause overheating. This led many investigators to search for polishing solutions with the effectiveness of perchloric acid and without the danger in handling. Young and Brytczuk (37) found that phosphoric-sulfuric acid mixtures produced high reflectivity on stainless steel. These mixtures are non-explosive and free from obnoxious fumes. The most effective bath was composed of 60 per cent phosphoric acid, 20 per cent sulfuric acid and 20 per cent water. Silman (31, p. 100) found that for mild steels a solution of wider range of operation was obtained by adding cresolsulphonic acid to the usual phosphoric-sulfuric acid solution.

Due to the efforts of many investigators there are today a varied number of electrolytes which are effective on most of the common metals without being dangerous to use. Such baths as sulfuric-phosphoric, sulfuric-phosphoric-chromic, and phosphoric-chromic acids are easily handled and control methods have been well worked out. Another bath of recent discovery (28) composed of chromium oxide, acetic acid and water has shown great effectiveness on steel. This is very easy to prepare and to use.

During the early days of the development of electrolytic polishing most of the investigators devoted their efforts to the

development of new solutions but little attention was given to the design and improvement of the electrolytic circuit. Lately some investigators have attempted to design simple circuits which are easy to arrange and do not require constant attention. Horowitz and Maltz (19) have designed a simple circuit which does not require attention after one minute of operation, requires the same setting for different size specimens, and maintains operational stability at higher voltages. Their circuit is like the conventional one but contains in addition a variable resistance. Zmeskal (40) and Brown and Jimison (3) have designed very simple circuits by using dry cells as the source of direct current. These circuits are simple to arrange and can be set up in a relatively small space. These circuits are particularly adaptable to polishing small specimens, and for this reason are very useful for metallographic purposes.

At the present time electrolytic polishing is an established process which is solving a variety of production problems (5, 11). Electropolishing is practically without competition in its ability to polish shapes whose surfaces are almost inaccessible to a wheel. Such products as gears and welded aircraft hoods can be polished in their innermost recesses with a finish as satisfactory as can be produced on any other area (11). One of the most generally employed of present applications of electropolishing on a commercial scale is in the manufacture of aluminum reflectors. There are two well known processes of polishing aluminum for this purpose; the Brytal process (31, p. 103) which uses an

alkaline electrolyte consisting of sodium carbonate and trisodium phosphate maintained at a temperature of 165 to 190° F., and the Alzak process which uses various acid electrolytes, the most common of which is fluoboric acid.

There are some difficulties which have yet to be overcome. The high current densities, which are generally required, demand large sources of current so that the conductors must be of large dimensions. The equipment is of necessity subjected to severe conditions on account of the corrosivity of the solutions. Temperature control also becomes a problem where high current densities are involved.

PURPOSE

There were two purposes in doing this research. The first purpose was to determine whether an electrolyte composed of chromic oxide, acetic acid and water would polish copper, nickel, sterling silver, alpha brass, or tin bronze to any appreciable extent.

The second purpose was to determine electrolyte compositions which at selected combinations of current density and time would polish these metals enough to attain a reflection equivalent to 95 per cent or better of that of a stainless steel mirror. A stainless steel mirror was used as standard of comparison.

EXPERIMENTAL PROCEDURE

Equipment

The equipment used in this problem consisted of an electrolytic unit, Plate I, and a reflectometer, Plate II.

The reflectometer consisted of a Weston photoelectric cell, a 6-volt bulb and a variable resistance, all enclosed in a box. The light from the bulb was focused on a hole which was drilled on one of the sides of the box. When this hole was covered by any reflecting surface, the reflected light struck the photoelectric cell which indicated the amount of light reflected. The photoelectric cell could be set at any desired reading by means of the variable resistance. A variation in resistance caused a change in voltage which in turn caused a change in the brilliancy of the bulb.

The electrical portion of the electrolytic unit, Plate III, consisted of a variable autotransformer, 0 to 130 volts capacity; a voltmeter, 0 to 50 volts capacity; and two ammeters, 0 to 1 and 0 to 5 amperes capacity. The other portion of the unit, called electrolytic cell, consisted of a glass crystallizing dish and a stainless steel cathode, Fig. 1. The cathode area was approximately 33 square inches.

Solutions

A total of 97 solutions were tested. The composition of these solutions was evenly scattered within the range of solubility of chromic oxide in acetic acid and water, Plate IV.

Specimens

The polishing capacity of the solutions was tested with commercially pure copper, commercially pure nickel, sterling silver, alpha brass, and tin bronze. The approximate composition of the bronze was 87 per cent copper, 10 per cent tin and 3 per cent zinc.

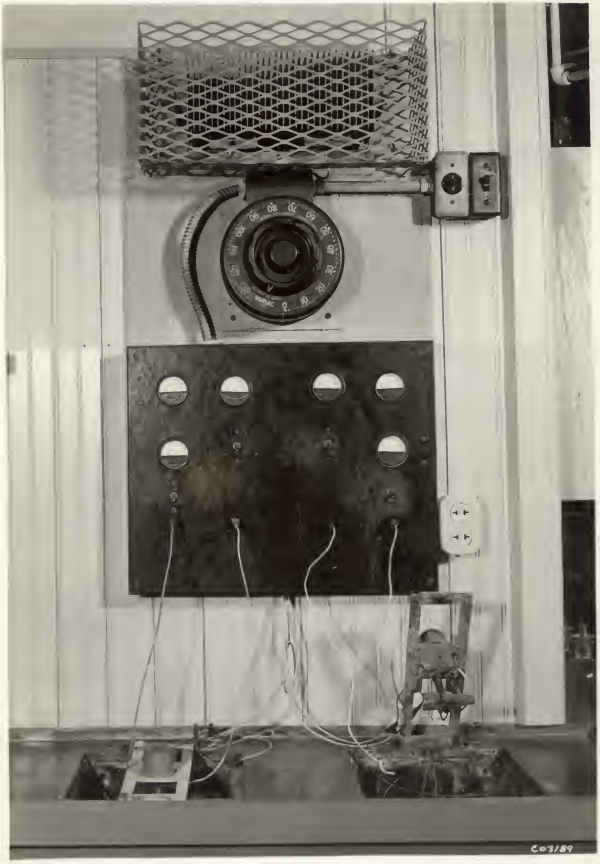
Procedure

The area to be polished on every specimen was standardized to 0.2 $inch^2$ and held parallel to the cathode at an approximate distance of 0.25 inch. The specimen was rotated at a speed of one revolution per second around a circle of approximately 1 inch radius. The surface to be polished was prepared by grinding it through 3/0 grit emery paper. The electrolyte was kept cool during each run in a bath of circulating water, Fig. 1, whose temperature varied from 16 to 17° C.

The solutions were tested under different current density-time conditions. For each current density the time was varied, in increments of 10 seconds, from 10 to 60 seconds or until

EXPLANATION OF PLATE I

Electrolytic unit with two cells.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EXPLANATION OF PLATE II

Reflectometer and stainless steel mirror.

PLATE II

EXPLANATION OF PLATE III

Wiring diagram of the electrolytic unit.

AC- Alternating current

T- Variable transformer

R- Selenium rectifier

S- Switch

F- Fuse

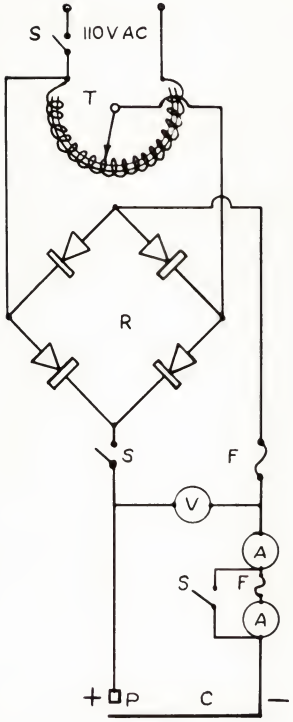
V- Voltmeter

A- Ammeter

P- Specimen (anode)

C- Cathode

PLATE III



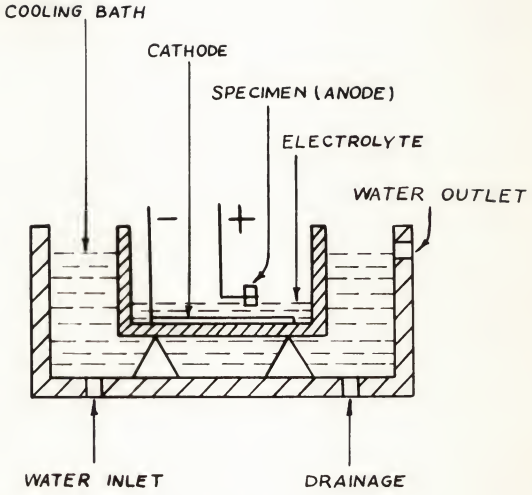


Fig. 1. Electrolytic cell with cooling bath.

polishing or pitting was observed. When polishing or pitting was not observed after 60 seconds, the time increments were increased to 30 seconds. When either of these was observed, the time increments were reduced to 5 seconds; then, the solution was tested within the limits of time at which polishing or pitting started. The current densities varied, in increments of 0.5 ampere per square inch to a value at which pitting made it impractical to continue or to a maximum of 15 amperes per square inch.

To evaluate the polishing ability of the electrolyte, the amount of light reflected by the polished specimen was used as criterium. In order to have a standard of comparison, the reflectometer was previously set to read 100 against a stainless steel mirror. In this way, the reflection of the specimen was measured in percentage of the reflection of the mirror. Before measuring the reflection, the specimen was washed with alcohol and dried with dry compressed air. Reflections of less than 50 per cent were not recorded because these reflections were often obtained by the grinding operation alone.

RESULTS AND CONCLUSIONS

None of the solutions tested were effective in polishing sterling silver, nickel, or bronze. Under all conditions of time and current density, the sterling silver developed a red film, presumably silver chromate, over the entire surface exposed

to the electrolyte. After removing this film no evidence of polishing was observed. All the solutions pitted bronze and none seemed to operate on nickel.

Several solutions operated satisfactorily on copper and brass, Plate V. Reflection values as high as 115 and 110 per cent of standard were obtained for copper and brass, respectively. The surface of the stainless steel mirror seemed to the eye to be more lustrous than that of the polished copper or brass, but the reflection of the latter two metals was higher because the photo-electric cell is more sensitive to the red and yellow light.

The compositions of the solutions which operated satisfactorily on copper and brass are illustrated on Plates VI and VII.

In the solutions of high water content the conductivity was high. Low voltages had to be used with these solutions to prevent excessive current densities. In the solutions of high chromic oxide or acetic acid content the conductivity was low, consequently high voltages were required to obtain sufficient current densities to polish the specimens.

It can be concluded that electrolytes composed of chromic oxide, acetic acid and water do not polish sterling silver. Unless an agent is added to prevent the formation of the silver chromate, the metal cannot go into solution. Within the limits of the experimental conditions, it can be concluded that such electrolytes are inoperative on nickel and bronze. The results prove conclusively that certain proportions of chromic oxide, acetic acid and water polish copper and brass satisfactorily.

EXPLANATION OF PLATE IV

Acetic acid-chromic oxide-water phase diagram.

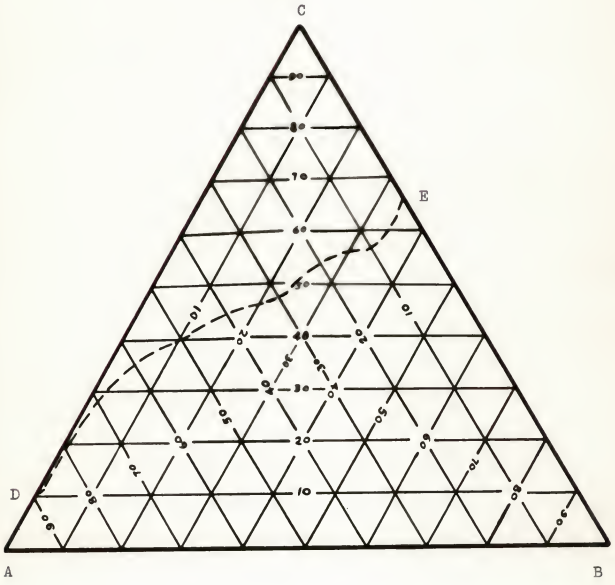
A- 100 per cent acetic acid

B- 100 per cent water

C- 100 per cent chromic oxide

The dotted curve D-E indicates the limit of solubility of chromic oxide in acetic acid and water.

PLATE IV



EXPLANATION OF PLATE V

A- Mechanically polished copper; the operation took 35 minutes.

B- Electrolytically polished copper; the operation took 10 seconds.

C- Specimen A after being etched.

D- Specimen B after being etched.

E- Mechanically polished alpha brass; the operation took 35 minutes.

F- Electrolytically polished alpha brass; the operation took 5 seconds.

G- Specimen E after being etched.

H- Specimen F after being etched.

All magnifications 212 x.

Etchants

For copper:

(percentages by weight)

3.60 per cent chromic oxide

0.67 per cent ammonium chloride

6.72 per cent nitric acid

8.21 per cent sulfuric acid

80.80 per cent distilled water

For alpha brass:

(percentages by volume)

23.0 per cent hydrogen peroxide

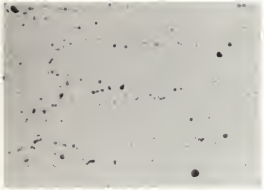
38.5 per cent ammonium chloride

38.5 per cent distilled water

PLATE V

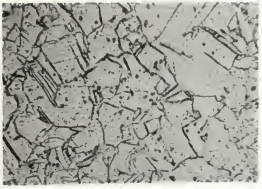
A

E

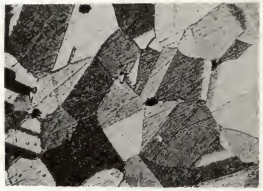


B

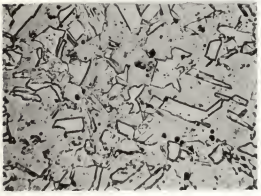
F



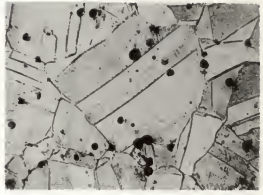
C



G



D



H

EXPLANATION OF PLATE VI

Acetic acid-chromic oxide-water phase diagram.

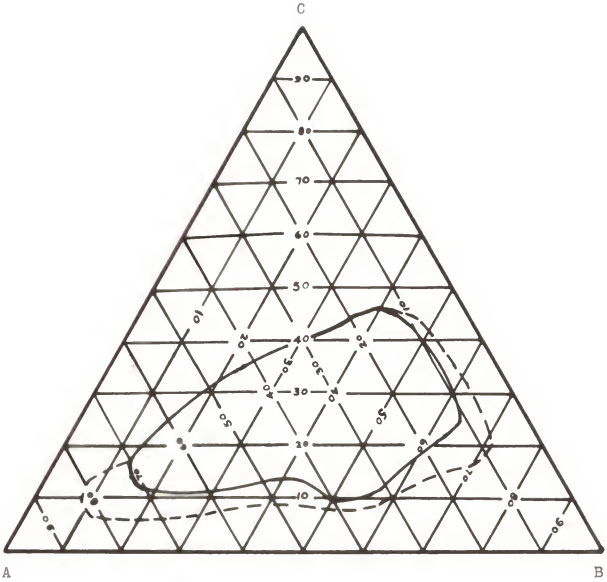
A- 100 per cent acetic acid

B- 100 per cent water

C- 100 per cent chromic oxide

The solutions which give the best results on copper fall on the area included by the solid curve. The solutions which fall on the area included by the dotted curve polish copper but not satisfactorily.

PLATE VI



EXPLANATION OF PLATE VII

Acetic acid-chromic oxide-water phase diagram.

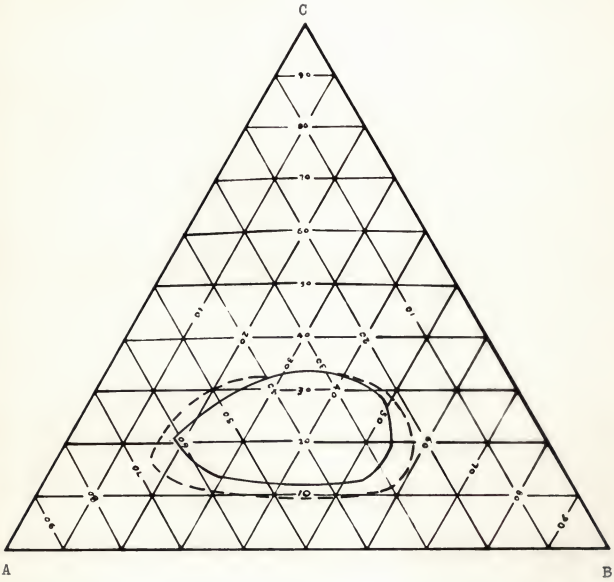
A- 100 per cent acetic acid

B- 100 per cent water

C- 100 per cent chromic acid

The solutions which give the best results on alpha brass fall on the area included by the solid curve. The solutions which fall on the area included by the dotted curve polish alpha brass but not satisfactorily.

PLATE VII



ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor G. A. Sellers and Dr. A. E. Hostetter for their assistance in choosing this problem, and in securing the necessary equipment, and to Dr. A. E. Hostetter and Mr. Dale E. Zabel for their useful suggestions and assistance in interpreting the results.

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ABSTRACT

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The second purpose was to determine electrolyte compositions which at selected combinations of current density and time would polish these metals enough to attain a reflection equivalent to 95 per cent (or better) of a stainless steel mirror which was used as standard.

An electrolytic unit was set up consisting of a full wave selenium rectifier, a variable autotransformer, two ammeters, a voltmeter, a stainless steel cathode and a glass crystallizing dish.

The polishing ability of 97 solutions was tested with copper, nickel, sterling silver, alpha brass, and tin bronze.

The composition of the solutions was evenly scattered within the range of solubility of chromic oxide in acetic acid and water. Every solution was tested with each metal at different current density-time combinations.

The degree of luster of the specimens was evaluated by the amount of light reflected by their polished surfaces. A stainless steel mirror was used as standard of comparison.

None of the solutions polished sterling silver, tin bronze, or nickel. The sterling silver developed a red film, presumably

silver chromate, which prevented any polishing action from taking place; nickel seemed to be unaffected and tin bronze was pitted.

Several solutions operated satisfactorily on copper and brass. Reflection values as high as 110 and 115 per cent of standard were obtained for brass and copper, respectively. The range of variation of the constituents of the solutions which gave the best results on alpha brass was smaller, indicating that a smaller number of solutions can be used on this metal. The constituents of these solutions varied from 25 to 60 per cent acetic acid, 12 to 35 per cent chromic oxide and from 18 to 55 per cent water.